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Nano- and Microstructures in Chemistry Electrochemistry, and Materials Science

by

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We have recently become interested in the fabrication and characterization of ensemble of nano- and micro-scale structures. In contrast to the majority of the work in this area, our interests do not lie in the microelectronic applications of such structures; rather, we are interested in the possible electrochemical, chemical, optical, and materials applications of nanostructure ensembles. We review these applications and the results of our investigations in this paper.

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Nano- and Microstructures in Chemistry, Electrochemistry, and Materials Science[1]

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INTRODUCTION

We have recently become interested in the fabrication and characterization of ensembles of nano- and micro-scale structures. In contrast to the majority of the work in this area, our interests do not lie in the microelectronic applications of such structures; rather, we are interested in the possible electrochemical, chemical, optical, and materials applications of nanostructure ensembles. We review these applications and the results of our investigations in this paper.

EXPERIMENTAL

The general procedure used in this laboratory for preparation of ensembles of nanostructures entails electrochemical deposition of metals or plastics into the pores of a microporous filtration membrane (1-5). The key point is that the pores of the host membrane act as templates for the nascent nanostructures. This procedure is shown schematically in Figure 1. Details can be found in references (4,5). We have used this procedure to prepare Pt, Au and electronically conductive plastic nanocylinders with diameters as small as 10 nm (see e.g. Figure 2).

As indicated in Figure 1, membranes with discrete, straight-through micro- or nanopores form the basis of our fabrication methods. These membranes are prepared by tracking and etching plastics (6,8) or by anodizing Al (7). The track-etched plastic (8) and anodized Al (Anopore (7)) membranes are commercially available.

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RESULTS AND DISCUSSION

Ultramicroelectrodes are electrodes which have at least one characteristic dimension which is smaller than ca. 10 μm. The most obvious example is a disk with a diameter which is 10 μm or smaller. Because ultramicroelectrodes offer electrochemists a myriad of opportunities that are not possible at electrodes of conventional dimensions, ultramicroelectrodes are of considerable current research interest (4,9-11). We have used the procedure outlined in Figure 1 to prepare ensembles of Pt and Au ultramicrodisk electrodes with diameters as small as 50 nm.

One of the most exciting potential applications of ultramicroelectrode ensembles is in the area of chemical sensors. Theory predicts, and we have experimentally demonstrated, that such ensembles can electrochemically sense significantly lower concentrations of electroactive analyte molecules than can electrodes of macroscopic dimensions. That is, put in the jargon of analytical chemistry, ultramicroelectrode ensemble-based sensors show lower detection limits than analogous sensors based on conventional electrodes.

The lower detection limits displayed by ultramicroelectrode ensembles are illustrated in Figure 3. Figure 3A shows a calibration curve associated with the electrochemical detection of an Fe-containing ion at a conventional carbon paste electrode. The detection limit at this conventional electrode is ca. 300 nM. Figure 3B shows the analogous calibration curve at an ultramicroelectrode ensemble. The detection limit at the ultramicroelectrode ensemble is ca. 30 nM. Thus, the ultramicroelectrode ensemble shows a one order of magnitude enhancement in detection limit relative to the conventionally-sized electrode (9,10).

Metal films thicker than several hundred angstroms are usually opaque to visible and infrared radiation. However, manipulating the microstructure of metal films can produce transparency. Effective medium theory predicts that electrically disconnected metal particles which are small relative to the wavelength of the incident light will be transparent (12). This effect occurs when the optical electric field produces a screening charge at the metal-dielectric boundaries. This charge excludes the electric field from the particle and "squeezes" the light into the non-absorbing dielectric between the particles.

The optimal microstructure for transparency to unpolarized light is an ensemble of nanocylinders with their axes oriented parallel to the incident light rays (12). The strategy outlined in Figure 1 was used to prepare an ensemble of transparent metal nanocylinders (5). Gold nanocylinders were electroplated into a silver-backed Anopore (Figure 3B) membrane. The silver was then dissolved, leaving electrically isolated, 200 nm-diameter gold cylinders imbedded in an Anopore membrane. The gold that fills the pores makes up 65% of the gold/Anopore composite surface.

The fourier transform infrared spectrum of an Au/Anopore composite membrane is shown in Figure 4. This spectrum was corrected for the Anopore absorption. At wavelengths greater than ca. 6 μm the composite membrane transmits ca. 75 % of the incident photons. If the Au microstructures were opaque, only ca. 20 % of the light would pass through the membrane. Thus, in agreement with the predictions of effective medium theory, these nanostructures are optically transparent.

A number of plastics are now known which conduct electricity via an electronic mechanism similar to conduction in metals (13). In most cases, however, the conductivities observed are significantly lower than metallic conductivities. We have recently discovered that when electronically conductive plastics are synthesized within the pores of nanoporous host membranes, dramatically enhanced conductivities are observed (14).

Figure 5 shows an example of the conductivity enhancements observed. Figure 5 is a plot of conductivity along polypyrrole or poly(3-methylthiophene) fibers vs. the diameter of the fiber. The large diameter fibers show conductivities roughly equivalent to the conductivities of conventional polypyrrole or poly(3-methylthiophene) (i.e. 10 to 100 S cm^{-1}). However, fibers with diameters on the order of 10's of nm's show dramatically higher conductivities. In the case of poly(3-methylthiophene) a ca. two-order of magnitude enhancement in conductivity is observed.

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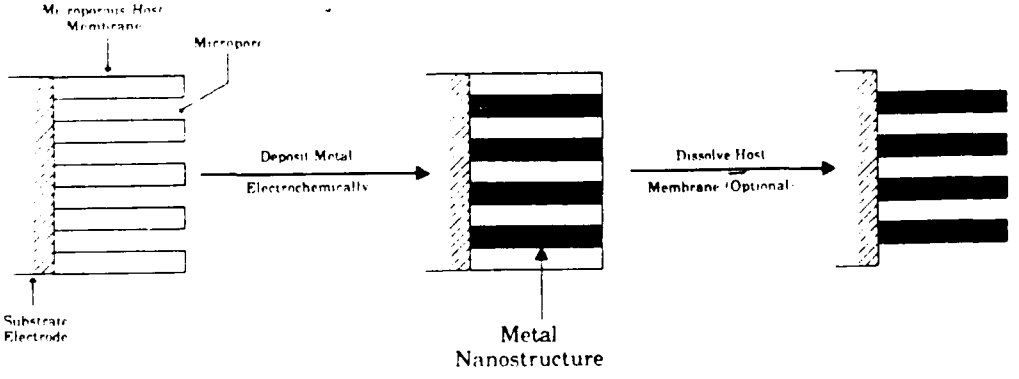

Fig. 1. General approach for preparing ensembles of micro- and nanostructures.

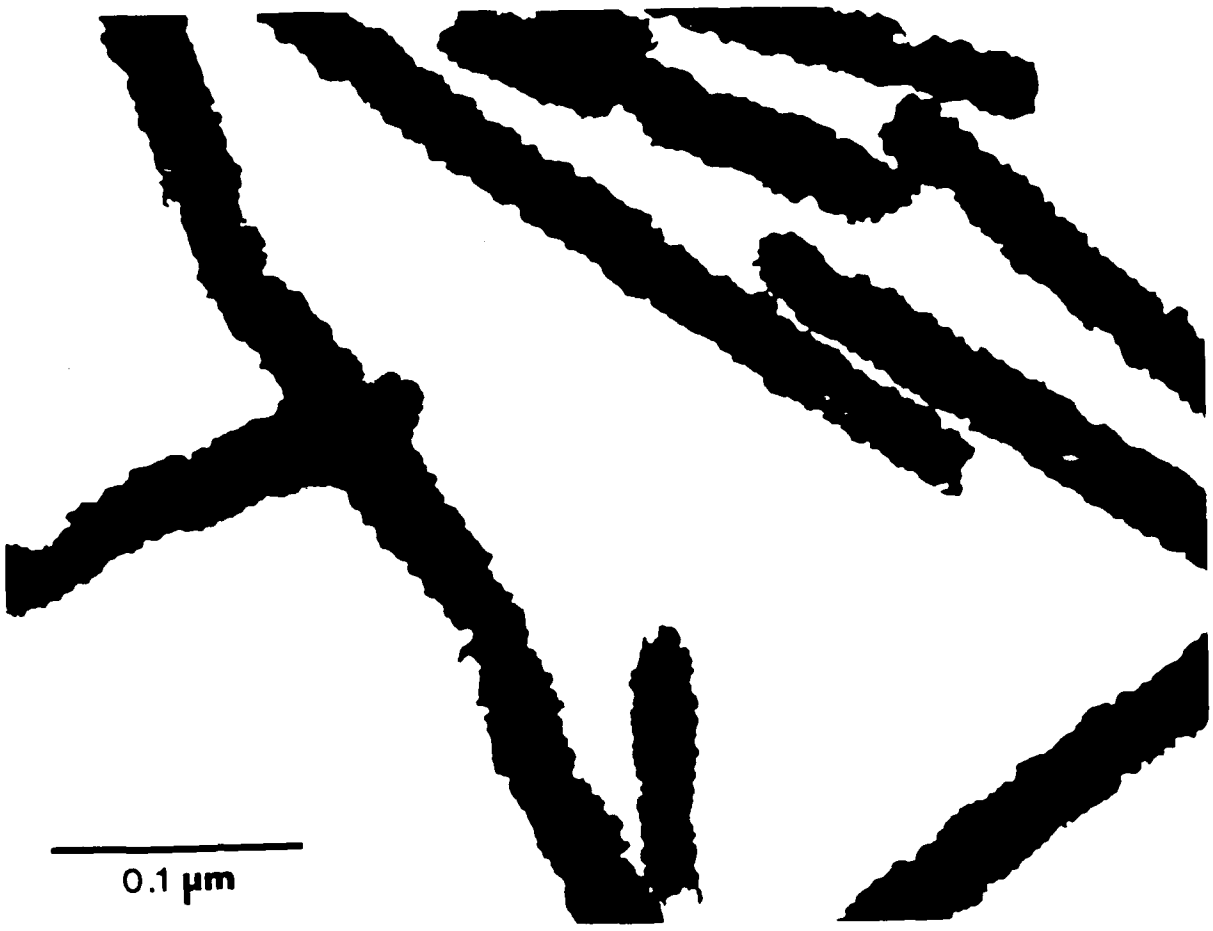

Fig. 2. TEM of 300 angstrom diameter platinum wires.

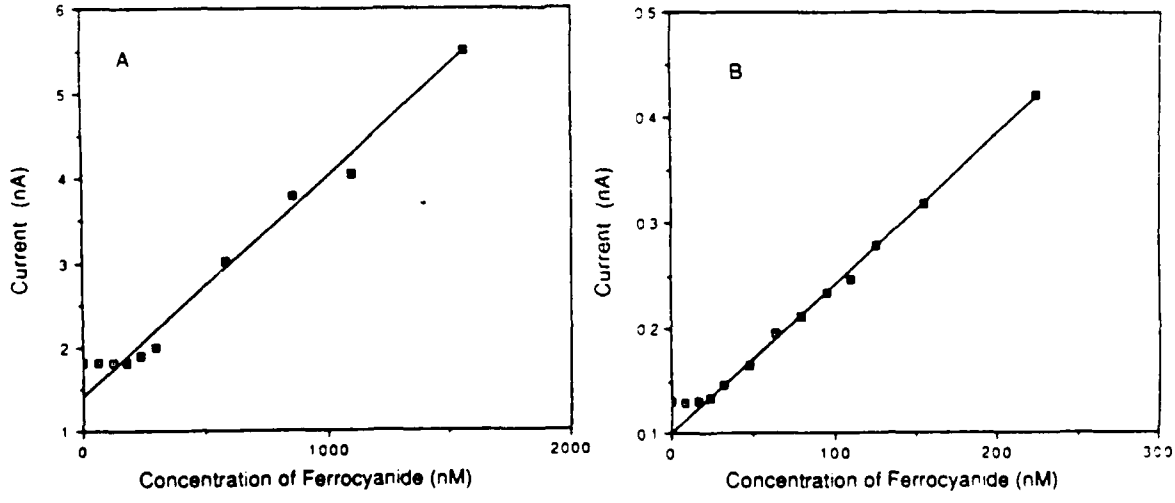

Fig. 3. Calibration curves showing the limit of detection for $Fe(Cn)_6^{4-}$ at (a) a macro-sized electrode and (b) an ultramicroelectrode array.

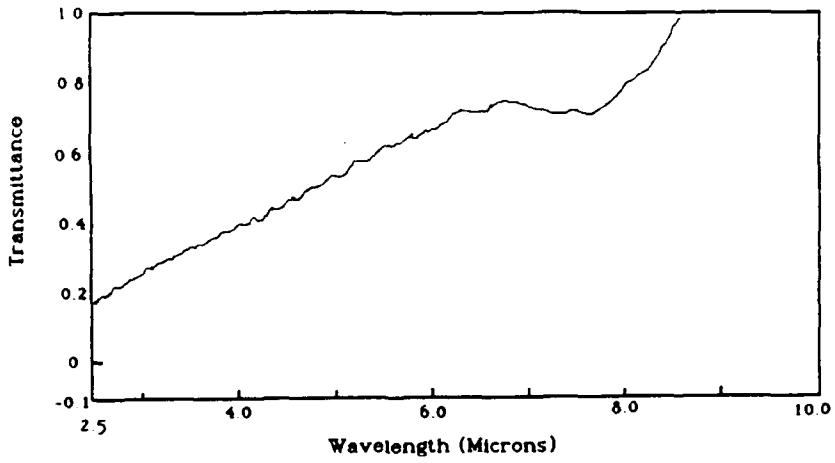

Fig. 4. A fourier transform infrared spectrum of a gold/Anopore composite (spectrum of Anopore subtracted).

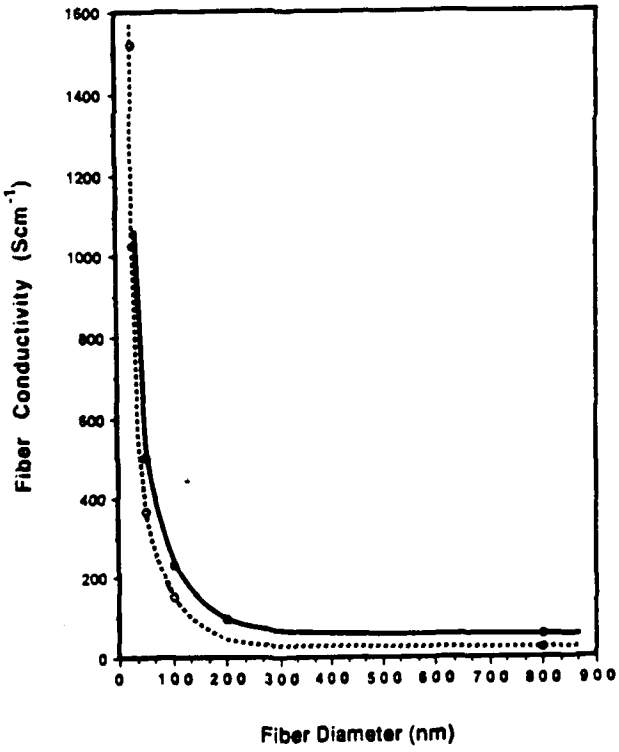

Fig. 5. Plot of conductivity of conducting polymer fibers vs. fiber diameter. Poly(3-methylthiophene) (dashed line). Polypyrrole (solid line).